Summary (Effect of Ethanol and MtBE on BTEX Biodegradation in the Saturated Zone: Kinetic Studies)

There is substantial knowledge about many of the mechanisms affecting saturated zone transport of gasoline containing ethanol. Microbially-mediated processes appear to dominate the fate and transport of gasoline components in the presence of ethanol, but additional research was needed to better understand the impact that ethanol may have on benzene, toluene, ethylbenzene, and xylene (BTEX) biodegradation kinetics. The research presented in this chapter found that:

1. <u>BTEX and ethanol were typically degraded more rapidly in microcosms that used previously contaminated aquifer material, although previous exposure did not always result in high degradation activity</u>.
2. <u>Methyl tertiary butyl ether (MtBE) was not degraded within 100 days under any conditions, and did not affect BTEX or ethanol degradation patterns</u>.
3. <u>Ethanol was typically degraded before BTEX compounds, and had a variable effect on BTEX degradation as a function of electron-accepting conditions and bacterial source.</u> This is best illustrated with toluene, which was the most commonly degraded of the BTEX compounds. In some cases, ethanol retarded toluene degradation, but it occasionally enhanced toluene degradation in microcosms with electron acceptors supplied in excess. This enhancement may be attributable to the fortuitous growth of toluene-degrading bacteria during ethanol degradation.

As part of this study, aquifer columns were also used to characterize ethanol, MtBE, and BTEX migration and biodegradation in a flow-through system simulating natural attenuation. The results from these column studies indicate that:

- <u>Both ethanol and MtBE could enhance dissolved BTEX mobility by exerting a cosolvent effect that decreases sorption-related retardation.</u> This effect, however, is concentration-dependent and was not observed when ethanol or MtBE was added (at 1%) continuously with BTEX to sterile aquifer columns. However, a significant decrease in BTEX retardation was observed with 50% ethanol, suggesting that neat ethanol spills in bulk terminals could facilitate the migration of pre-existing contamination.
- <u>The preferential degradation of ethanol and the accompanying depletion of oxygen and other electron acceptors suggest that ethanol could hinder the natural attenuation of BTEX plumes.</u> Using non-sterile columns packed with soil material, ethanol (106 mg/L) was degraded rapidly and exerted a high demand for nutrients and electron acceptors that could otherwise have been used for BTEX degradation. MtBE (9 mg/L), on the other hand, was not degraded and did not affect BTEX degradation.

The results presented in this chapter are particularly important for the fate of benzene, which is the most toxic and the most recalcitrant of the BTEX compounds under anaerobic conditions. Nevertheless, it is unknown to what extent ethanol would increase the distance that benzene

migrates before being attenuated to acceptable concentrations by natural processes. Therefore, the following studies should be conducted to quantify the effect of ethanol on plume length and improve our risk assessment capabilities:

- A controlled release and additional study of field sites: One major concern is that ethanol could increase the distance that BTEX compounds migrate before being attenuated to acceptable concentrations by natural processes. Nevertheless, there is considerable uncertainty regarding the magnitude and significance of this potential impact. Therefore, field-scale and modeling studies should be conducted to quantify the effect of ethanol on plume length. Such studies could include controlled-release (field) experiments and statistical analyses of LUFT site data with and without ethanol. Controlled-release studies should be multidisciplinary, and could benefit from incorporation of the microbial ecology technique developed for this project (Chapter 4, Beller *et al.*, 2001).
- Better integration of ethanol degradation kinetics into models: Mathematical fate and transport models should also be developed and calibrated to integrate the negative effects of ethanol on BTEX degradation (e.g., electron acceptor depletion and/or repression of BTEX metabolic flux) with potential positive effects (e.g., enhanced bacterial growth). Such models would be useful for risk assessment and management purposes.
- Improved anaerobic biostimulation strategies: Longer BTEX plumes represent a greater risk of exposure to potential downgradient receptors, which could result in decreased acceptability of natural attenuation as a remedial approach at some sites. This could stimulate a shift of cleanup decisions towards engineered remediation approaches. Although the most common engineered bioremediation approaches used for BTEX cleanup are aerobic, introducing sufficient oxygen to meet the high oxygen demand exerted by ethanol will likely be technically difficult and prohibitively expensive. Therefore, anaerobic biostimulation strategies should be considered. However, the lack of field experience with enhanced anaerobic bioremediation approaches for BTEX contamination will require the refinement and demonstration of suitable approaches. These could include the addition of nitrate to increase the electron acceptor pool (in a manner that does not create toxicity or clogging problems), and bioaugmentation with anaerobic cultures that can degrade benzene, which is relatively recalcitrant under anaerobic conditions.
- Improved characterization of methane, and volatile fatty acids at ethanol release sites: Neat ethanol spills and some gasohol releases could pose an explosion risk when site-specific conditions favor extensive methanogenesis and methane accumulation. In addition, ethanol-derived acetate and other volatile fatty acids could cause a decrease in pH (thus hindering biodegradation processes) and create taste and odor problems. Therefore, site characterization protocols should include methane and volatile fatty acid analyses near the source zone. Aesthetic impacts to groundwater quality could also be created by reductive dissolution of iron and manganese caused by metal-reducing bacteria feeding on ethanol. Therefore, dissolved metal analyses should also be considered.